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(Article begins on next page)



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# Inter-annual and seasonal variability in PM10 samples monitored in the city of Turin (Italy) from 2002 to 2005

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## **Abstract**

The temporal trends of ten elements, namely Cl, Cu, Cr, Fe, Mg, Ni, P, S, Zn and Zr, in airborne particulate matter sampled in the urban area of Turin (Piedmont, Italy) were determined by wavelength dispersive X-ray fluorescence for the period from 2002 to 2005. The average daily concentrations were as follows: Cl 322 ng/m<sup>3</sup>; Cr 16.4; Cu 8.19 ng/m<sup>3</sup>; Fe 274 ng/m<sup>3</sup>; Mg 1501 ng/m<sup>3</sup>; Ni 7.33 ng/m<sup>3</sup>; P 19.8 ng/m<sup>3</sup>; S 1206 ng/m<sup>3</sup>; Zn 333 ng/m<sup>3</sup> and Zr 8.15 ng/m<sup>3</sup>. Some elements, namely Al, Ba, Ca, K, Na, Si and Sr, were not quantifiable using XRF because of the too high contribution from the filter blank.

A clear seasonal pattern with higher concentrations of most of the elements in the cold periods was observed. Moreover, no marked change in the element distribution in atmospheric particulate matter over the four years was evidenced during the sampling period, to indicate that similar sources have influenced the elemental composition of it in these last years. The application of multivariate chemometric techniques (Principal Component Analysis and Hierarchical Cluster Analysis) to the experimental results allowed us to identify correlations among the investigated elements and to reveal similarities and differences between sampling sites.

## **Keywords**

PM10; Turin (Piedmont Region, Italy); Elements in PM10; Principal Component Analysis; Hierarchical Cluster Analysis

## **1. Introduction**

Atmospheric pollution resulting from airborne particulate matter, especially PM10 (aerodynamic equivalent diameter less than 10 µm) fraction, continues to be a major problem despite remarkable improvements having been made in terms of air quality over the last decades, thanks to the adoption of several measures like the introduction of fuels with lower environmental impact, the technological advancements in the energy civil and industrial sectors and the introduction of petrol-run vehicles equipped with catalytic converters and low-emission diesel engines into the market.

Indeed, the PM10 fraction of the airborne particulate matter can be considered as the carrier of many harmful elements (such as Cr, Cu, Ni, Pb, S, V and Zn) that can be deposited into the human respiratory system and thus cause respiratory and cardio-vascular pathologies [1-3].

In general, sources of particulate matter in the air are both natural (e.g. wind-blown sand, sea spray, volcanic ash, etc.) and anthropogenic (e.g. industrial facilities, incineration, household

heating, transportation, etc.). The environmental impact of anthropogenic sources is regarded to be more significant than that of natural sources.

Epidemiological studies have established a linkage between the concentration of the inhalable (PM<sub>10</sub>) and respirable (PM<sub>2.5</sub>) fractions and their elemental concentration with adverse respiratory health effects. As a result, Ministerial Decree (MD) 02/04/2002 [4], acknowledged from European Community (EC) Directive 1999/30/EC [5], introduced in Italy a daily limit and an annual average limit of 50  $\mu\text{g}/\text{m}^3$  and 40  $\mu\text{g}/\text{m}^3$  respectively for PM<sub>10</sub>, both taking effect as of 01/01/2005.

In recent years Directive 2004/107/EC [6] determined specific target values (with effect as of 1 January 2013) for the presence of several chemical elements, namely arsenic, cadmium and nickel, and of benzopyrene in PM<sub>10</sub>.

Nowadays it has become very important to know the elemental composition and the sources of the airborne particulate matter, in order to identify possible emergency situations in the environment resulting from bad air quality and consequently take action and implement recovery plans specific for the problems encountered.

In this study we determined the concentrations of ten elements (Cl, Cu, Cr, Fe, Mg, Ni, P, S, Zn and Zr) by wavelength dispersive X-ray fluorescence (WD-XRF) in airborne PM<sub>10</sub> samples collected at two sampling sites in Turin city, Piedmont Region (Italy), one localised in the centre and the other in the outskirts of the town, from 2002 to 2005. Based on our measurements, we attempted to characterise the pollution status of the study area and to make some assumptions about the possible emission sources of particulate matter taking into account both the spatial, seasonal and annual variations in concentration levels and the results of statistical analysis. This study is the result of a cooperation between the University of Turin, the Polytechnic of Turin and the regional agency for environmental protection (ARPA Piemonte).

## **2. Material and methods**

### *2.1. Sample collection and weighing*

PM<sub>10</sub> samples were collected in two sampling stations located in two different areas of Turin: CR station is in Consolata Road, in the historical center of the town; AR station is at the intersection between Paolo Veronese Road and Reiss Romoli Road, on the northern outskirts of the town, in an area of high density vehicular traffic (Figure 1). It is expected that the two sampling stations are affected by different emission sources because near CR station the traffic is mainly constituted by a limited car circulation, whereas AR station is subjected both

to heavy vehicular traffic, involving cars and trucks, being close to an highway, and to various industrial emissions, since several plants (foundries, plastic material stamping, etc.) are present in its neighborhood. Among the available samples, which were collected daily, 96 specimens were selected for this study: forty eight samples originated from CR station, one per month for the years 2002, 2003, 2004, 2005, and another 48 originated from AR station, one per month for the same years. We have considered the PM<sub>10</sub> samples that fall between the 5° and 95° percentile calculated on the PM<sub>10</sub> concentrations for each year. Subsequently, for each month, those samples having the highest quantity of particulate were chosen for analysis.

The samples were taken using low volume air samplers for 24 h. PM<sub>10</sub> was collected on glass fibre filters (total diameter 47 mm, diameter of the deposition area 38 mm) at a flow rate of 2.3 m<sup>3</sup> h<sup>-1</sup>. The total volume of air passing through a filter was computed using a flow recorder. The flow control was carried out in the actual condition mode.

The concentrations of PM<sub>10</sub> were measured by weighing each filter before and after sampling on an analytical balance in a controlled atmosphere (20 °C, 50 % relative humidity) according to MD 02/04/2002 [4].

## *2.2. Element determination*

The contents of the elements in PM<sub>10</sub> samples were determined by WD-XRF, with a ZSX Rigaku wavelength dispersive XRF instrument; the following crystals were used as dispersing elements: LiF, Ge, penta-erythritol (PET), thallium acid phthalate (TAP). Taking the available crystals into account, all elements with an atomic weight less than 9 were excluded from the analysis; therefore, also nitrogen and carbon, whose trends would be significant, could not be determined.

WD-XRF analysis of atmospheric particulate matter (considered to be homogenous in every part) is extremely rapid. The analysis is completely non-destructive in that no type of sample preparation is required, therefore there is no alteration of the material analysed.

The filters were placed on the sample holder and directly analyzed. Some blanks (i.e. clean glass fibre filters) were analysed by the same procedure to evaluate their average contribution in the samples analysis. In this way it was possible to evidence that Al, Ba, Ca, K, Na, Si and Sr were not quantifiable using WD-XRF because of the too high contribution from the filter blank.

### 2.3. Chemometric elaboration

The statistical-chemometric elaboration of the experimental data by Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA) was performed with XLStat 2007.3 software package. Data sets on the two sampling stations were autoscaled separately. When concentrations were below the detection limit, particularly for 2002 and 2003 years, a random value between zero and that limit was inserted in order to be able to thoroughly apply PCA and HCA without losing any data; this procedure was used in other studies, e.g. by Chan et al. [7].

PCA is a multivariate chemometric technique used to obtain a synthetic representation of experimental data that brings to light correlations between variables considered and similarities present among samples analysed. This technique makes it possible to extract the most information possible contained in a set of multivariate data, summarising it in a few linear combinations of the variables [8,9].

The interpretation of the PCA results can be facilitated through the graphic representation of loading plot and of score plot; in particular, the loading plot allows one to understand the relationships between the variables (in this case the different elements determined in PM<sub>10</sub>), emphasising their positive and negative correlations and the role of each variable in the different components; the score plot enables the valuation of behaviour of the objects (in this case the samples of particulate analysed) towards the different components and their similarities or differences.

The aim of HCA is to group data by similarity, taking into account all the information contained in the data set and not only a part of it, as in PCA. Similarity close to 100% indicates high resemblance between the objects, while deviations from a value of 100% indicate differences. Objects that are most similar are "fused" into a single group or cluster and the calculation of similarity is iteratively repeated. The calculation is interrupted when the minimum similarity (maximum dissimilarity) between the objects has been established.

Various graphical means exist to evaluate the aggregation in a cluster, but the most widely used is the dendrogram, which highlights not only the various clusters, but also their distance. The level of aggregation of the units or clusters is visualised in ascending order. Hierarchical Cluster Analysis can be run in the Q-mode, in which clusters of samples are sought, or in the R-mode, where clusters of variables are desired [8,9].

HCA is an effective statistical method for qualitative study of the composition of atmospheric aerosol and can be used to identify the groupings of variables not well detectable only with PCA.

### **3. Results and discussion**

#### *3.1. PM10 concentrations*

Figure 2 shows the concentrations of PM10 in the 96 samples investigated.

Despite different environmental situations, the samples taken at the two atmospheric sampling stations revealed no substantial difference in terms of PM10 concentrations.

It is possible to observe that PM10 presents a typical seasonal trend, with higher concentrations in the winter months, that is, when meteorological conditions (in particular thermal inversion) reduce vertical circulation, thereby lowering the mixing layer thickness and promoting the accumulation of suspended particles at low levels in the atmosphere. Another cause of the periodicity of the data is surely attributable to the use of household heating systems due to the lowering in temperature. Indeed the conversion of emissions from motor vehicles and from household heating systems into particulate matter is stimulated at low temperature [10]. This behaviour was observed also by other researchers in other sites in the North of Italy [11,12].

#### *3.2. Element contents*

The average concentrations as well as the minimum and maximum values of all the elements analysed in PM10 are shown in Table 1 for all the years considered and both the sampling sites; the results have been reported also separating the hot season (from April to September) from the cold one (from October to March). The temporal trends of element concentrations in the samples are shown in Figure 3.

It is notable that lead resulted below the detection limits in all the samples examined over a period of 4 years; therefore, if present in PM10, its concentration was only at trace or ultra-trace level. This result, being referred to particulate matter in an urban environment, is in agreement with the gradual elimination of leaded petrol in motor vehicles since the 1980s.

Although the PM10 concentration did not show relevant variations over the course of four years, the element concentrations were below the detection limits of WD-XRF in the PM10 originating from both sampling stations for some samples collected in 2002 (namely for all elements in January, February, April and May) and for a few samples collected in 2003 (namely for all elements for April and only for Cu from March to July). Furthermore, comparing the PM10 samples from the two sampling stations in the year 2005, one can deduce that the element concentrations monitored at CR are, on average, greater than those



monitored at AR for most of the elements considered. This difference between the two stations presently remains unexplained.

Unfortunately the sensitivity of the WD-XRF technique did not allow us the determination of some elements in atmospheric particulate matter because its detection limits are usually higher than those of ICP atomic emission spectrometry, ICP mass spectrometry, graphite furnace atomic absorption spectrometry or energy dispersive XRF. However, it must be borne in mind that the principal advantages of this analytical method is that it is reliable, non-destructive, and the measurements are quite easy to perform and rapid. Moreover, by this instrument it was possible to determine some potentially toxic elements, like Cr, Cu, Ni and Zn.

We examined the temporal trends of the concentrations of the determined elements. The trends observed for chlorine and iron are typically seasonal, with significantly higher concentrations during the winter months. This finding is true for both CR and AR sampling stations. These results underline the unquestionable role of meteorology in the evolution of pollutant concentrations in air, in particular in orographically complex zones such as the Alpine arc encircling the north-west of the Piedmont Region. In some cases, when the thermal inversion is very severe and the "Foehn" winds are weak, the air recirculation in lower valleys is limited and, especially in winter, episodes of urban pollution, sometimes very intense, may occur.

With regard to chromium, copper, nickel and zinc concentrations, an approximately seasonal trend is evident, with minimal summer concentrations and higher levels in the winter months or, for some years, in spring, for both CR and AR sampling stations.

On the other hand, the other elements determined, i.e. magnesium, phosphorous, sulphur and zirconium, did not display so clear seasonal trends, with the exception of phosphorous and sulphur in 2005; furthermore the concentrations of these elements in 2005 were higher than for other years (2002-2004). Due to the lack of information on meteorological conditions, it is not possible to establish if this increase was caused by differences in temperatures and/or humidity in 2005 compared to the other years.

The presence of relevant concentrations of sulphur also in the summer months from 2002 to 2004 can be explained considering that its concentration in atmospheric particulate matter should mostly be due to secondary sulphates, deriving from the oxidation of SO<sub>2</sub> emitted on a regional scale primarily by power plants and industries, originated at a greater extent in climatic conditions with elevated irradiation. In fact, oxidizing species (OH, HO<sub>2</sub> radical

species), that quickly oxidize sulphur dioxide, are generated from photo-chemical reactions and therefore are present in higher concentrations in periods of extended irradiation [13].

Moreover, an increase of sulphate in the summer season may be due to meteorological conditions, characterised by high temperatures and humidity: in fact, it has been calculated that, at medium latitudes, over 65% of tropospheric sulphate is formed in cloud droplets following oxidation reactions in the aqueous phase [14]. Finally it is possible to surmise that the atmospheric circulation is more efficient on regional scale in the spring-summer period and, hence, an higher concentration of sulphate from various regional sources (production of thermo-electrical energy, emissions from industrial activity, etc.) can be transported into the study area to contribute to the formation of secondary aerosol.

These phenomena could explain the significant presence of sulphates in atmospheric particulate matter, both in the summer and winter months, even though one would expect a greater production of SO<sub>2</sub> in the winter period in a city such as Turin, where gas oil heating systems still exist. It is reasonable to presume that the increased anthropogenic contribution of SO<sub>2</sub> in the winter months is balanced by a greater influence of photochemical and meteorological processes in summer.

The trend observed for phosphorous in atmospheric particulate matter is similar to that of sulphur, i.e. with constant concentrations during the whole year with the exception of 2005, in which the concentrations of these elements result higher in winter months. Phosphorous is generally present in atmosphere as phosphate. One source of P is anthropogenic, since this element is present in motor oils as a component of wear-resistant additives. A natural source of P is soil dust.

The concentrations of magnesium and zirconium vary randomly during the sampling period and a well-defined trend is not observable; this behaviour is not unexpected considering that these two elements are mainly of crustal origin.

Table 2 shows a comparison of the average elemental concentrations (ng m<sup>-3</sup>) for PM<sub>10</sub> in Turin with those in other Italian towns. The element distribution in Turin atmospheric particulate matter is similar to that of the other considered towns, taking into account the great variability present in these data, with the exception of Mg and S. These elements are present in higher concentrations in Turin. Regarding sulphur, this behaviour can be explained with the emission of SO<sub>2</sub> by gas oil heating systems in winter and by power plants and industries, at a regional scale, in the summer period. As to the behaviour of magnesium, it is not possible to find an explanation at the present time.

### 3.3. Chemometric data handling

In an effort to identify the possible sources that influence the chemical composition of PM<sub>10</sub> and to highlight spatial and temporal differences, the chemometric treatment of the experimental data was carried out through the application of two well-known statistical multivariate analysis techniques: Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA). The chemometric study was carried out both on the whole data set (96 samples with 10 variables) and considering the analytical data on the two sites separately.

Figure 4 shows the combined plot of scores and loadings obtained by PCA considering the samples collected in CR site. Taking into account the scree plot, we have reported only the first two principal components that contain a total variance of about 90 %; all the others PCs contain a very low, and therefore not significant, percentage of information.

An evident differentiation exists between the samples collected in the hot period (from April to September) and in the cold one (from October to March): the former are grouped in a single well-compacted cluster to indicate a greater similarity, while the latter form two separated clusters that extend along the two directions of the PC1 and PC2. This distribution is due to the seasonal trend and to the differences among the investigated years discussed above: the samples collected in hot period are characterised by lower concentrations for all the elements considered; the samples collected from October to March 2005 and some samples collected in the cold period of the other years are characterised by high concentrations of Ni, Cr, Fe and Cu, suggesting a higher input of pollutants due to thermal inversion; finally most of the samples collected in the cold periods in 2003 and 2004, namely CR-Sep-03, CR-Oct-03, CR-Nov-03, CR-Dec-03, CR-Jan-04, CR-Feb-04 and CR-Mar-04, are strongly influenced by the variable identified by the vector of Zr and partially by the variables identified by the vectors of Zn and Mg, characterised by an unlabeled seasonal trend.

Regarding variables, a clear correlation among Mg and Zn is evident, suggesting a common origin due to the input of road dust resuspended by vehicular traffic [18]. The correlation between Cr and Ni is very likely of anthropogenic origin, possibly due to industrial emissions transported by wind, even if the load in Ni is also related to traffic. The correlation among Fe, Cu, S, Cl and P is more difficult to interpret and might indicate an input from several sources (local traffic and/or fossil fuel combustion processes). Finally it is interesting to note that zirconium, a typically crustal element, is not correlated with other elements, confirming its different source.

The score and loading plot of the first two principal components, containing a total variance of about 80 %, for AR site is reported in Figure 5. First of all, also for this sampling station a clear differentiation between the samples collected in the cold period and in the hot one is evident: they take up opposite positions on PC1. In particular the samples collected from September to March 2005, together with some samples collected in the cold period in the other years, namely in November and December 2004, in January, February and March 2003, and in November 2002 are grouped in a single cluster aligned with the direction of the vectors representing typical markers of vehicular traffic (Ni, Fe and Cu), of fossil fuels combustion in heating systems (S) and of the use of NaCl to prevent ice formation on the roads in the winter months (Cl). The greater influence of the first two sources during the cold period can be attributed both to the thermal inversion and to the fact that the formation of atmospheric particulate matter from motor vehicles and from household heating systems is stimulated at low temperature, as already reported before. A second cluster is formed by the samples collected from January to April 2004 and by the AR-Nov-03 sample; it is strongly influenced by magnesium, which is considered a marker of the soil dust source. The higher contribution of this element in these months may be due to resuspension of local and regional dust, but also to long-range transport of dust from North Africa [19]. Finally the samples collected in the hot periods form two separate clusters, even if close to each other: one cluster includes the samples having negative scores on PC2, collected from June to September 2002 and from May to August 2005 along with samples AR-Dec-02, AR-Sep-04 and AR-Oct-04; the other cluster is constituted by the samples having positive scores on PC2, namely from May to September 2003 and from May to August 2004 along with samples AR-Dec-03 and AR-Oct-03. Both groups are characterised by low loadings for all the elements considered, in particular for Zr and Mg in the first cluster and for all other elements with the exception of P, Zn and Cr for the second one. This behaviour is a further confirmation of the seasonal trend discussed previously.

The dendrogram (Figure 6) obtained by Q-mode HCA considering the complete dataset shows again a separation between the samples collected in the hot period and in the cold one. In particular the samples collected in the cold period of 2005 and in the hot period of all years considered form very compact clusters. No outstanding difference in terms of sampling year and sampling station is observed: it is hence likely that the sources influencing the content of these elements in atmospheric particulate matter of Turin city did not greatly change from 2002 to 2004 and between two sampling stations. The similarity between the two stations

suggests that the seasonality is the most evident phenomenon that drives the element distribution in PM10 samples.

R-mode hierarchical cluster analysis was eventually applied to the total data matrix which enabled us to make hypotheses on the possible sources contributing to Turin atmospheric particulate matter, under the assumption that different levels of dissimilarity among elements are indicative of different sources of emission (Figure 7). For the identification of such sources we also took into account our knowledge on the features of the city of Turin. First of all it is evident that zirconium is a singleton, i.e. it is separated from all the others elements at the highest level of dissimilarity; this is a further confirmation of the strictly crustal origin of this element. A second cluster is characterised by more elements, namely S, Zn, Fe, Ni, Cu and Cr, that are linked at different levels of dissimilarity, suggesting that they do not derive from a single emission source but they are likely all emitted in atmosphere from several anthropogenic sources. In particular Fe, Ni, Cu and Cr, linked at a low level of dissimilarity, could represent the vehicular traffic source since they are usually associated with emissions from vehicles, like release by mechanical abrasion of metal structures of vehicles, engine components, tires and brake linings, besides vehicle exhausts [20,21]. This group is linked at a higher level of dissimilarity with Zn and this is compatible with the hypothesis that also this element partially derives from traffic, since its presence in the air is often associated to the resuspension of road dust by vehicular traffic. The link between S and the other elements included in the cluster at an higher level of dissimilarity suggests that they derive from more than one source. Indeed sulphur, despite its anthropogenic origin, is produced as secondary aerosol by fossil fuel combustion, metal smelting or other anthropogenic activities. Anyway, it is not possible to exclude some contribution from fossil fuel combustion processes for the other elements included in the cluster, particularly Cr and Fe.

The third cluster is characterised by a close link between Mg and P likely due to their possible origin from soil dust. Magnesium is usually considered as marker for this source; some researchers found higher concentration of phosphorous in rural sites than in urban sites [22], suggesting that its presence in the investigated samples could partly be due to resuspension and transport of soil dust by wind. Moreover, it is not possible to exclude some contribution from NaCl used as anti-freeze agent also for Mg, present as an impurity in this material. The link between this cluster and chlorine can be considered a confirmation of mixed origin for Mg and is likely due to the fact that chlorine does not have a strictly anthropogenic origin since it can be associated in atmospheric particulate matter to the use of sodium chloride to prevent ice forming on the roads.

#### **4. Conclusions**

From the study carried out, it was noted that the distribution of Cl, Cu, Cr, Fe, Mg, Ni, P, S, Zn and Zr in atmospheric particulate matter of the city of Turin has not markedly changed over the sampling period, i.e. from 2002 to 2005. This suggests that similar sources have influenced the elemental composition of airborne particulate matter in the city in these last years. On the contrary it is evident that both PM<sub>10</sub> and element concentrations in each year considered have a typical seasonal trend. This behaviour is common to that of atmospheric particulate matter in other sites in the North of Italy and it is mainly due to the thermal inversion that occurs in these regions during the winter.

The chemometric elaboration of experimental data allowed us to further confirm the seasonal pattern mentioned. Indeed the PM<sub>10</sub> samples are separated in all PCA plots depending on hot or cold sampling periods rather than on sampling year or site. Moreover, some possible sources influencing the content of the elements studied in atmospheric particulate matter of the investigated area were hypothesized by PCA and HCA.

Further studies, addressing a wider suite of analytes on a larger number of samples, are necessary to better identify and quantify the different emissive sources of PM<sub>10</sub> for the urban area investigated.

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## CAPTIONS TO FIGURES

Figure 1. Geographical map of Piedmont and details of the areas investigated.

Figure 2. Trends of PM10 concentrations collected in the atmospheric sampling stations of CR and AR in the years: 2002, 2003, 2004 and 2005.

Figure 3. Temporal trends of element concentrations in PM10 samples: a) Cl, Cr, Cu, Fe and Mg in CR station; b) Ni, P, S, Zn and Zr in CR station; c) Cl, Cr, Cu, Fe and Mg in AR station; d) Ni, P, S, Zn and Zr in AR station.

Figure 4. Combined plot of scores and loadings obtained by PCA considering the samples collected in CR station.

Figure 5. Combined plot of scores and loadings obtained by PCA considering the samples collected in AR station.

Figure 6. Dendrogram obtained by Q-mode CA considering the total data set (CR and AR stations). In bold: samples collected in the cold season (from October to March).

Figure 7. Dendrogram obtained by R-mode CA considering the total data set (CR and AR stations).

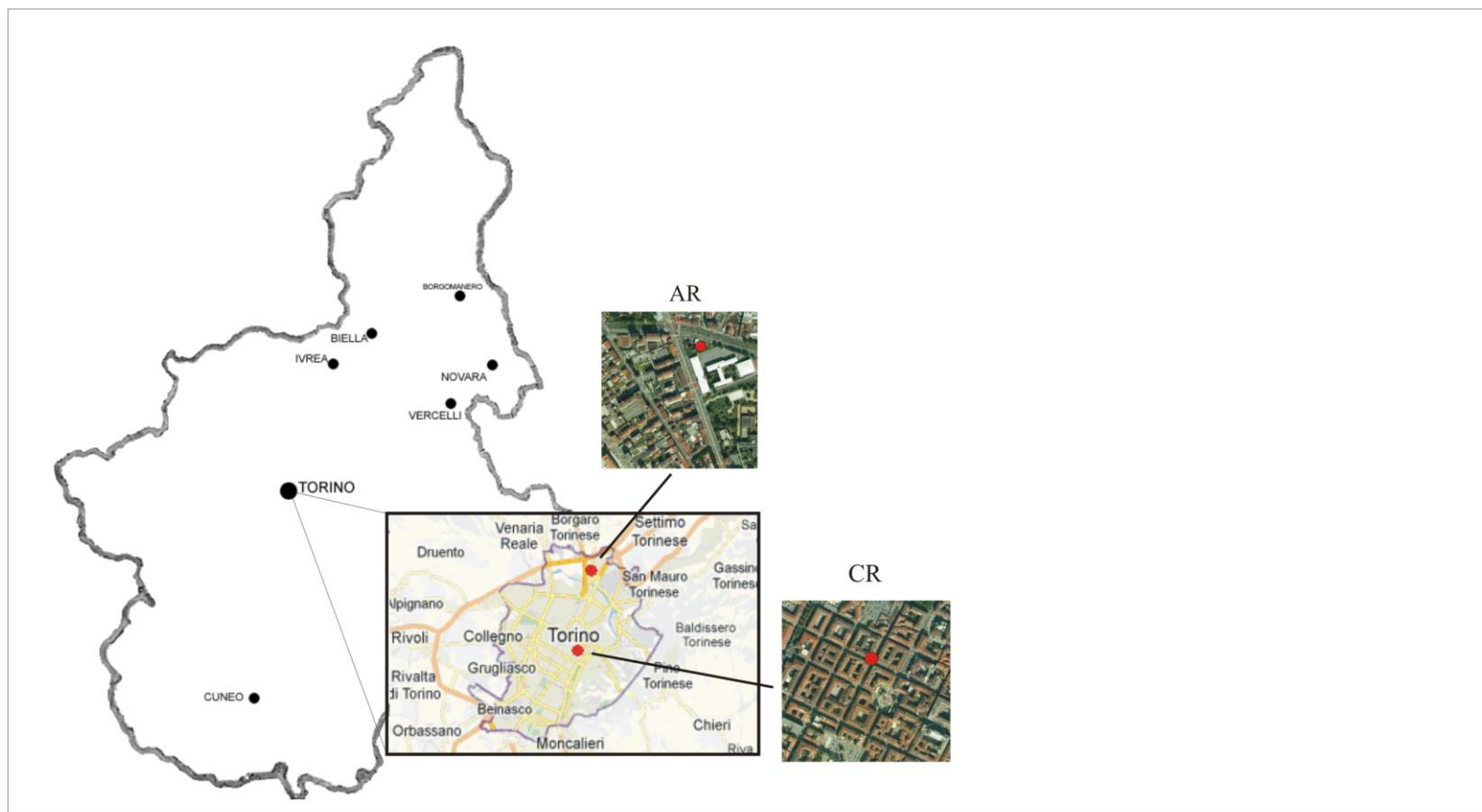


Figure 1

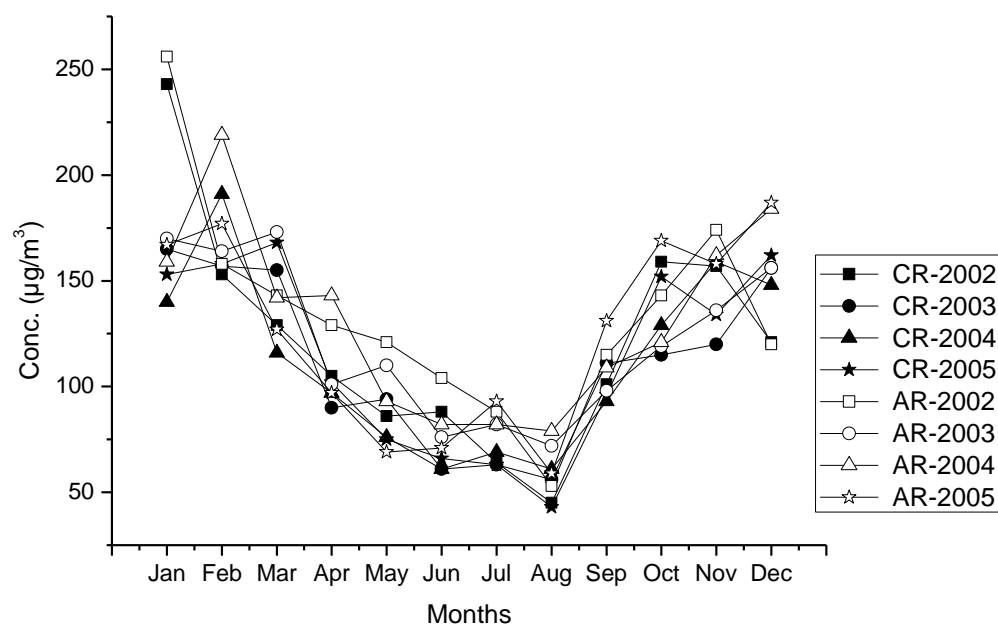
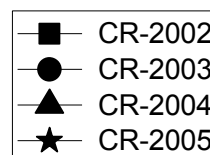
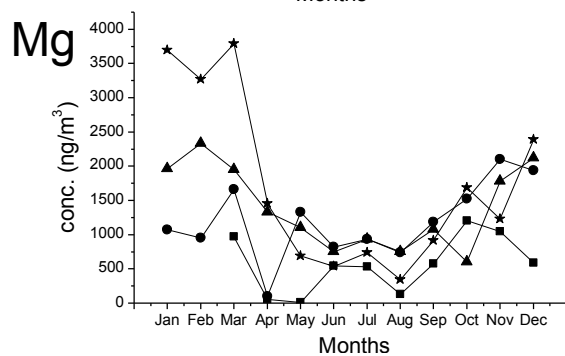
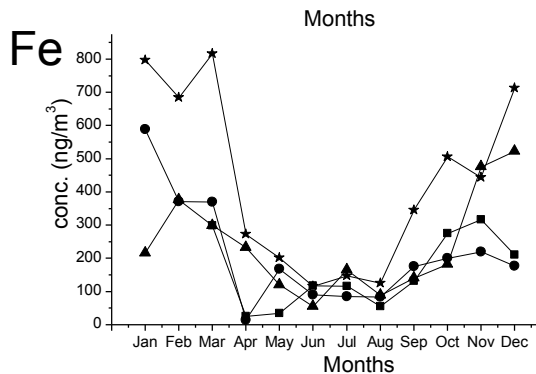
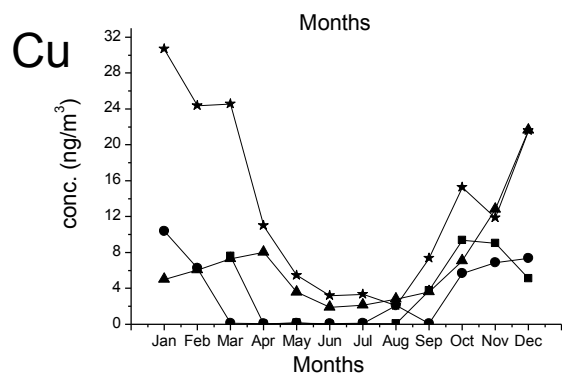
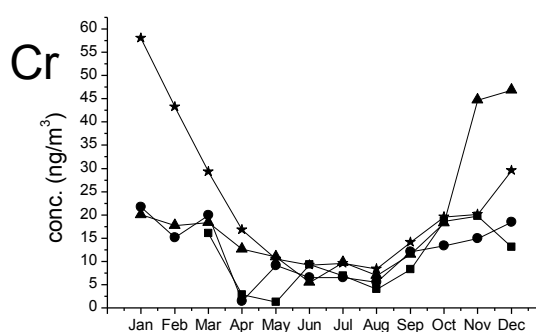
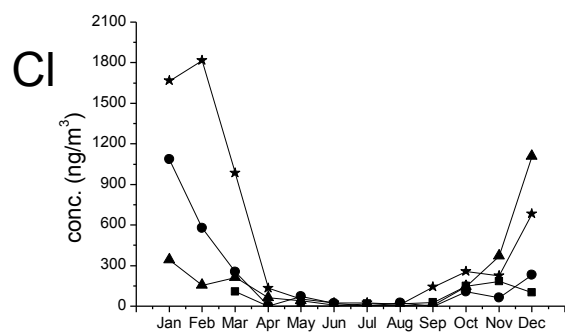


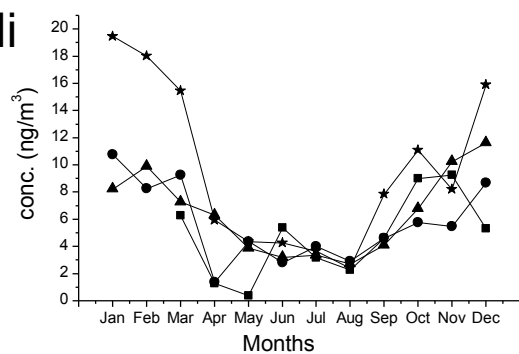
Figure 2

a)

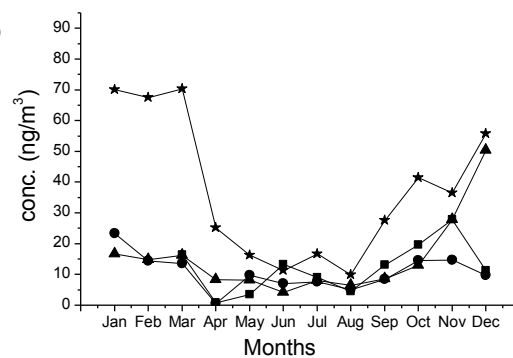


b)

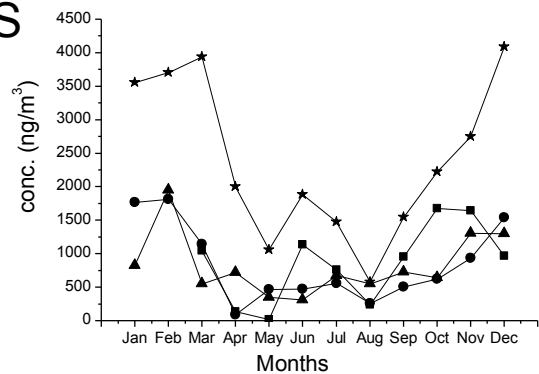
Ni



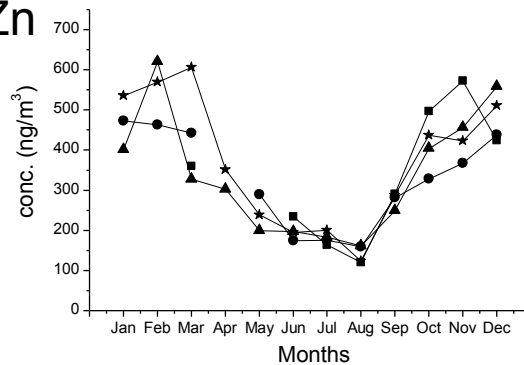
P



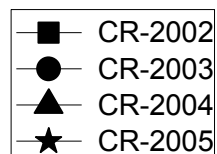
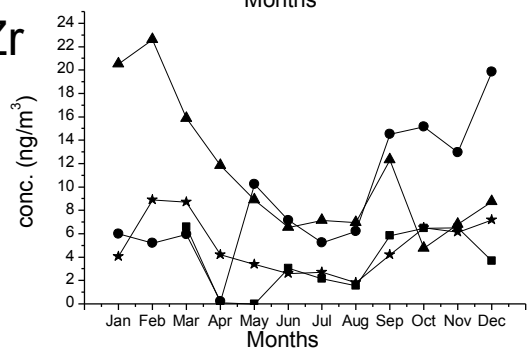
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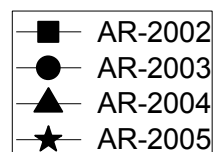
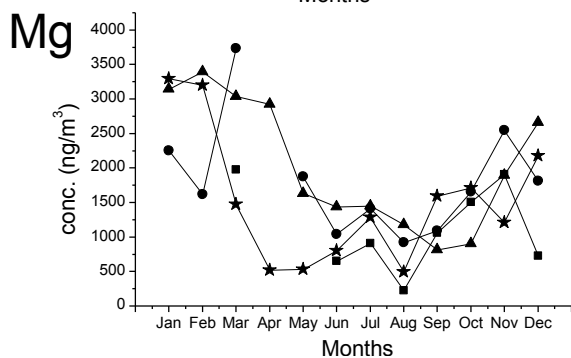
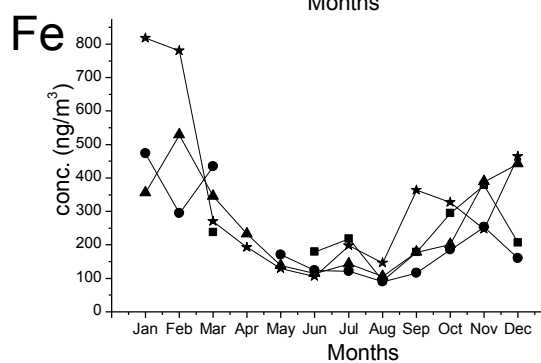
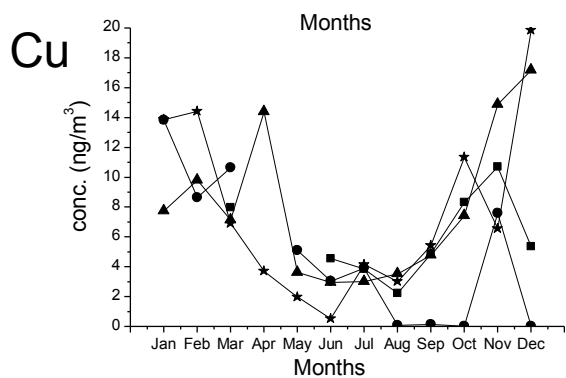
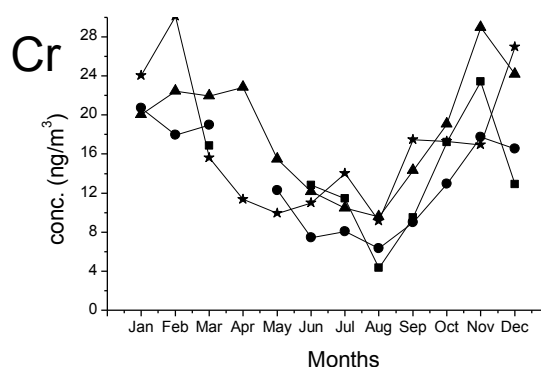
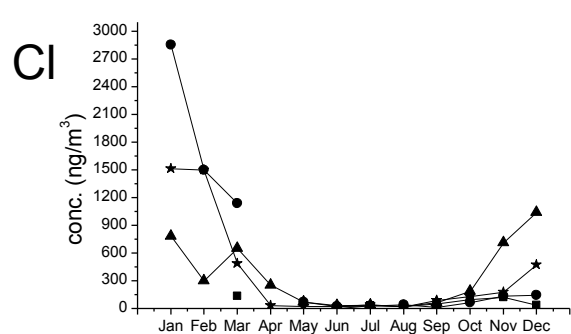
Zn



Zr



c)



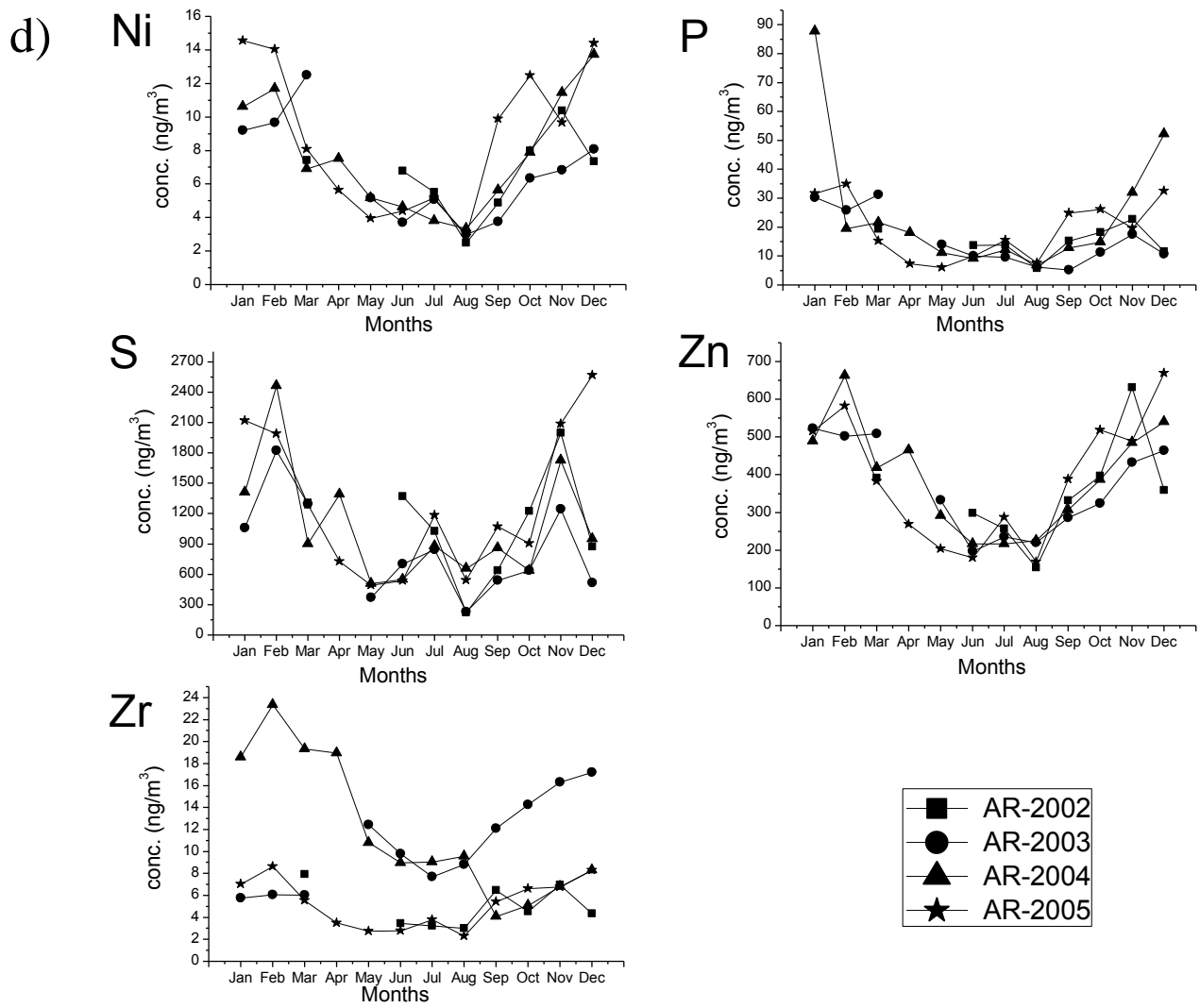


Figure 3

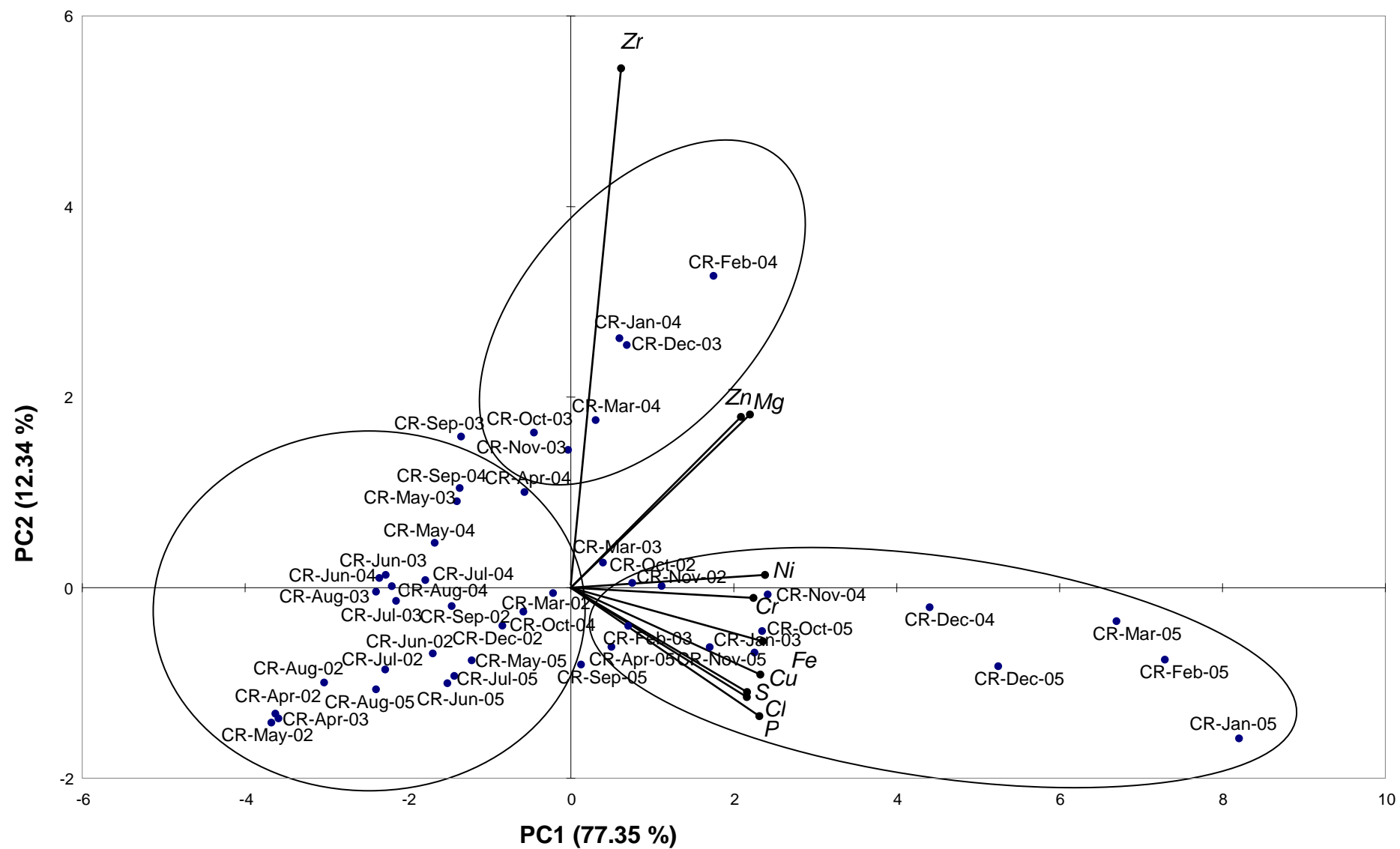


Figure 4





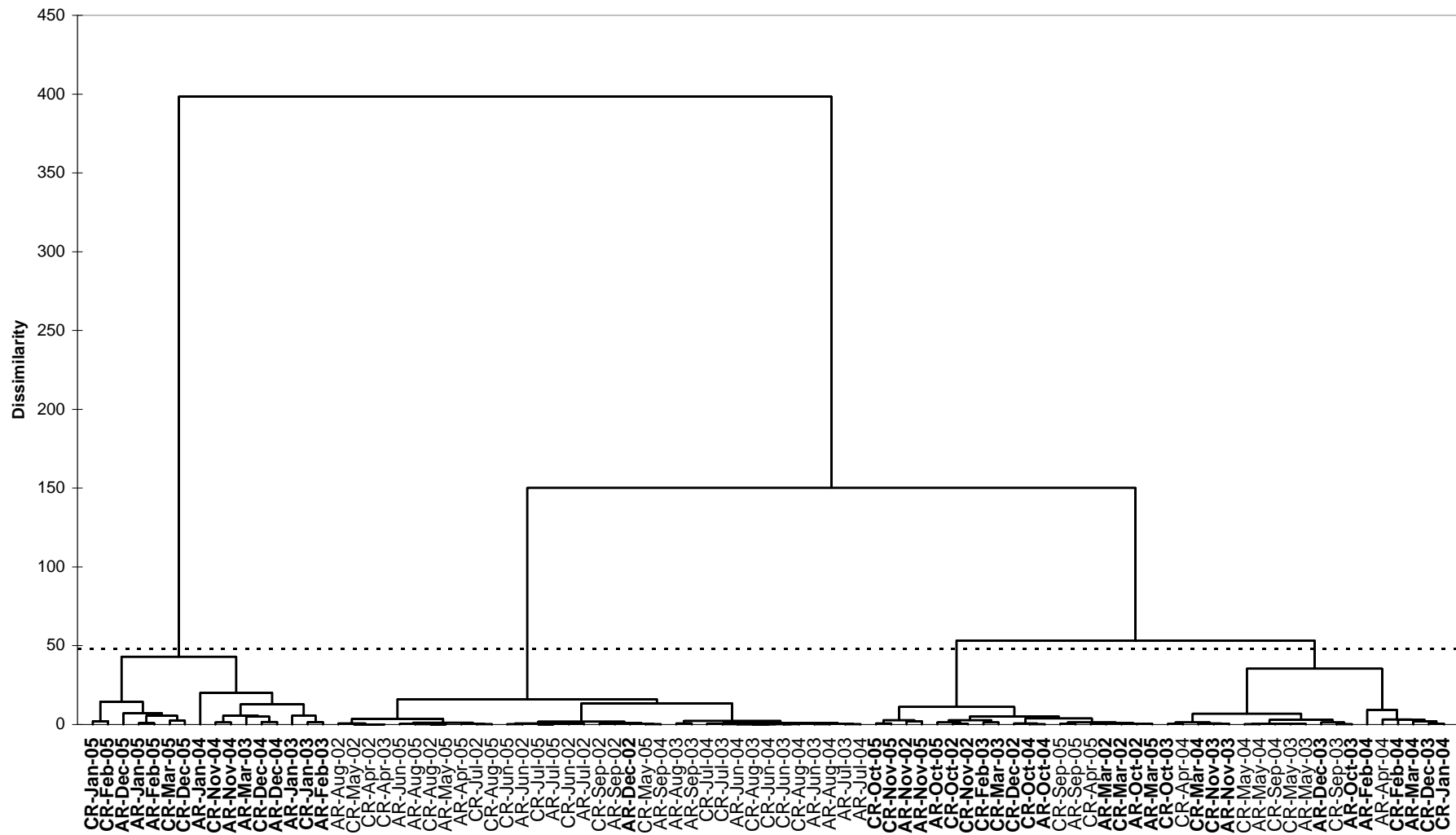


Figure 6

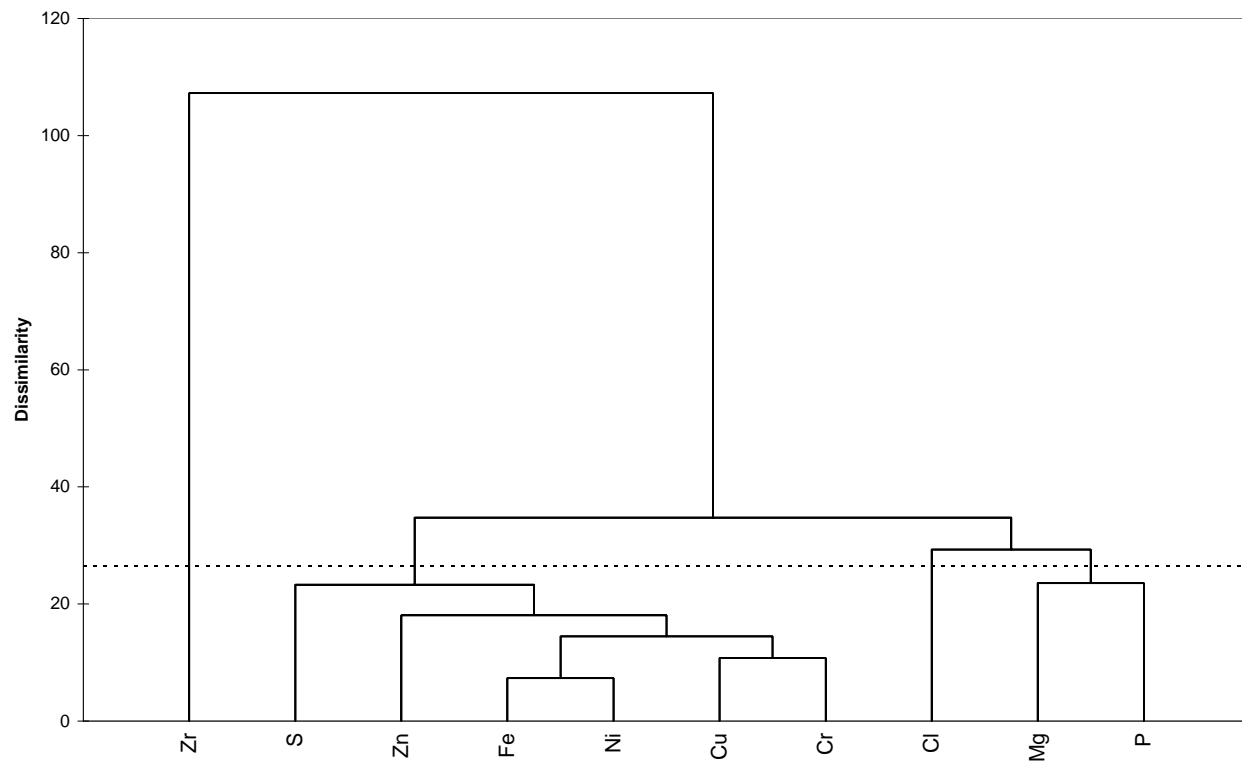


Figure 7

Table 1 Mean, median, minimum and maximum concentrations of each element determined in PM10 samples considering all the years and both the sampling sites for all seasons or separating the hot and the cold season. All values are expressed in ng/m<sup>3</sup>.

	All the periods				Hot season (April to September)				Cold season (October to March)			
	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max
Cl	322	107	3.31	2856	44.2	26.2	3.31	253	569	255	37.9	2856
Cr	16.4	15.1	4.08	58.1	10.3	9.72	4.08	22.8	22.3	19.3	12.9	58.1
Cu	8.19	6.90	0.51	30.7	4.22	3.64	0.51	14.4	11.4	9.03	5.03	30.7
Fe	274	209	55.5	818	152	135	55.5	364	390	351	160	818
Mg	1501	1306	132	3789	984	920	132	2923	1995	1902	588	3789
Ni	7.33	6.57	2.26	19.5	4.49	4.30	2.26	9.88	10.0	9.25	5.32	19.5
P	19.8	14.7	4.25	87.8	11.1	9.68	4.25	27.6	28.1	20.7	9.77	87.8
S	1206	962	221	4087	776	666	221	2006	1616	1306	520	4087
Zn	333	328	12.0	670	224	219	12.0	468	437	461	36.0	670
Zr	8.15	6.71	1.57	23.3	6.62	6.03	1.57	18.9	9.62	6.90	3.67	23.3

Table 2 Comparison of average element concentrations in urban PM<sub>10</sub> from different Italian towns. All values are expressed in ng/m<sup>3</sup>.

Element	Turin <sup>a</sup>	Milan <sup>b</sup>	Milan <sup>c</sup>	Palermo <sup>d</sup>	Genoa <sup>b</sup>	Florence <sup>b</sup>	Naples <sup>b</sup>
Cl	322	173			923	145	1060
Cr	16.4	7	13	6.5	7	9	7
Cu	8.19	19	72	49	12	37	16
Fe	274	391	1830	496	329	811	499
Mg	1501	127			224	165	244
Ni	7.33	2	10	5.5	2	3	2
P	19.8	29			28	29	29
S	1206	193			147	81	120
Zn	333	24	180	48	14	19	8
Zr	8.15		3		3	4	4

<sup>a</sup> This study, mean concentrations from Turin (2002-2005).

<sup>b</sup> D'Alessandro et al. (2003) [15].

<sup>c</sup> Vecchi et al. (2007) [16].

<sup>d</sup> Dongarrà et al. (2007) [17].